

US EPA ARCHIVE DOCUMENT



www.epa.gov/nrmrl

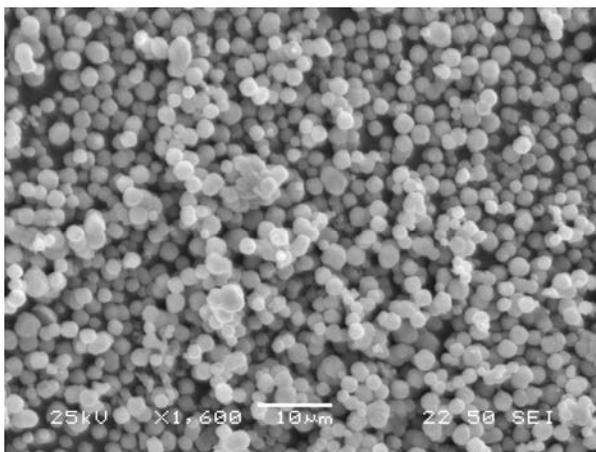
NRMRL

NATIONAL RISK MANAGEMENT RESEARCH LABORATORY
GROUND WATER AND ECOSYSTEMS RESTORATION RESEARCH

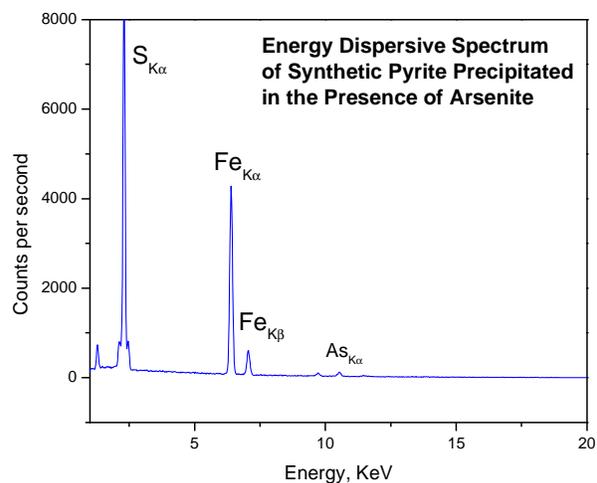
Natural Attenuation of Metals During Iron Sulfide Formation

Background and Objectives: Analyses of sediments have indicated a close association between the concentrations of iron sulfides and trace metals, yet there are few systematic investigations that explore the factors controlling trace element abundance in FeS and FeS₂, or conceptual models that describe impurity incorporation mechanisms. Three general processes have been proposed as important for controlling metal concentrations in reducing environments: 1) precipitation of pure metal (Me) sulfides; 2) formation of Me-Fe sulfide solid solutions by isomorphous substitution; and, 3) adsorption of trace metals onto the surfaces of iron sulfide particles. Many elements of environmental interest are found closely associated with iron sulfides including V, Cr, Mn, U, Co, Ni, Mo, Cu, Zn, As, Se, Ag, Cd, Sb, Hg, Tl, Pb, and Bi. The concentrations of these metals and metalloids within pyrite, for example, can be quite variable. In the case of As, pyrites with As contents approaching 8 to 10 wt% have been documented. Evidence for the pyrite-metal relationship is based mainly on indirect sequential extraction methodologies and direct microprobe measurements of relatively large pyrite grains. Questions remain concerning the influence of the geochemical environment on the processes of trace metal incorporation into iron sulfide phases, especially with respect to the relationship between mineral formation kinetics and metal uptake. This study evaluates the effects of nucleation rate and growth rate of pyrite on the uptake of metals, and specifically attempt to identify conditions where trace metal incorporation into pyrite is optimized.

Approach: The research approach involves laboratory experimentation and detailed analysis using a variety of wet-chemical and solid-phase characterization techniques.



Synthetic pyrite grains containing arsenic (SEM micrograph)



Principal Investigator: Richard Wilkin (U.S. EPA, Office of Research and Development, National Risk Management Research Laboratory, GWERD, Ada, OK 74820; 580-436-8874)

Collaborators: U.S. Geological Survey, Western Ecological Research Center, Auburn University

Accomplishments:

Wilkin, R.T. and Ford, R.G. (2002). Use of hydrochloric acid for determining solid-phase arsenic partitioning in sulfidic sediments. *Environmental Science and Technology*, v. 36, p. 4921-4927.

Wilkin, R.T., Wallschläger, D., and Ford, R.G. (2003). Speciation of arsenic in sulfidic waters. *Geochemical Transactions*, v. 4. 1-7.

Smieja, J. and Wilkin, R.T. (2003). Preservation of As(III) in sulfidic waters. *Journal of Environmental Monitoring*, v. 5, 1-5.

Wilkin, R.T. (2003). Metal sulfides in sediments. In *Encyclopedia of Sediments and Sedimentary Rocks*, ed. G. Middleton, p. 701-703, Kluwer Academic Publishers, The Netherlands.

Lee, M.-K., Saunders, J., Harrington, J., Lutes, C., and Wilkin, R.T. (2005). Geochemical modeling of arsenic speciation and mobilization: Implications for bioremediation. In: *Advances in Arsenic Research: Integration of Experimental and Observational Studies and Implications for Mitigation*, Eds: O'Day, P., Vlassopoulos, D, Meng, X, Benning, L., ACS Symposium Series Vol. 915, Ch. 29, p. 398-413. American Chemical Society, Washington D.C.

Wilkin, R.T. and Ford, R.G. (2006). Arsenic solid-phase partitioning in reducing sediments of a contaminated wetland. *Chemical Geology*, v. 228, 156-174.

Wilkin, R.T. and Bischoff, K.J. (2006). Coulometric determination of total sulfur and reduced inorganic sulfur fractions in environmental samples. *Talanta*, v. 70, p. 766-773.

Church, C., Wilkin, R., Alpers, C., and Rye, R. (2007). Microbial sulfate reduction and metal attenuation in pH 4 acid mine water. *Geochemical Transactions*, v. 8, 1-12.

Wilkin, R.T. (2008). Contaminant attenuation processes at mine sites. *Mine Water and the Environment*, v. 27, p. 251-258.

Beak, D., Wilkin, R., Ford, R., and Kelly, S. (2008). Examination of arsenic speciation in sulfidic water using x-ray absorption spectroscopy. *Environmental Science and Technology*, v. 42, p. 1643-1650.

Paul, C.J., Ford, R.G., and Wilkin, R.T. (2009). Assessing the selectivity of extractant solutions for recovering labile arsenic associated with iron (hydr)oxides and sulfides in sediments. *Geoderma*, v. 152, p. 137-144.